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ATMOSPHERIC EFFECTS OF CHEMICAL ROCKET PROPULSION

American Institute of Aeronautics and Astronautics

OCTOBER 1991
Final Report

AIR FORCE RESEARCH LABORATORY
AEROSPACE SYSTEMS DIRECTORATE
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7541
AIR FORCE MATERIEL COMMAND
UNITED STATES AIR FORCE

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14. ABSTRACT
This draft report is a summary of an AIAA workshop which identified and quantified the key environmental issues that relate to the effects on the atmosphere of rocket testing and use. Research detailed in this paper includes improving atmospheric modeling, data gathering, and methods for monitoring environmental changes. Also summarized in the paper is what is known about rocket propulsion testing and recommended plans to address and resolve some of the key issues. Areas looked at include stratospheric ozone depletion, acid rain, toxicity, air quality and global warming.

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ATMOSPHERIC EFFECTS OF CHEMICAL ROCKET PROPULSION

Report of an AIAA Workshop
Sacramento, California, June 28-29, 1991

AMERICAN INSTITUTE OF AERONAUTICS AND ASTRONAUTICS

WASHINGTON, DC

October 1, 1991

CONTENTS

OVERVIEW

The AIAA convened a workshop to identify and quantify the key environmental issues that relate to the effects on the atmosphere of rocket testing and use, and to recommend actions to resolve the issues. Communities represented at the workshop included rocket propulsion engineers, environmental scientists, environmental regulatory agencies, and environmental action groups.

Based on careful evaluation of scientific studies performed in the U.S., Europe, and the Soviet Union, the workshop concluded that the effects of rocket propulsion on stratospheric ozone depletion, acid rain, toxicity, air quality, and global warming were minuscule compared to other anthropogenic impacts. Nevertheless it was agreed that environmental concerns should become a major consideration in the design, development, and use of future rocket propulsion systems, and that every reasonable effort should be made to reduce undesirable environmental effects. Also, both the data and the analytical models used to reach conclusions on the effects of rocket propulsion on the atmosphere need substantial improvement to attain satisfactory confidence levels. Further, it was agreed that due to the global nature of the issues the necessary research, formulation of standards and regulations, and efforts to reduce environmental effects be conducted on an international basis.

Specific research areas detailed by the workshop include improving atmospheric modeling, data gathering, and methods for monitoring environmental changes. These improvements should focus

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on heterogeneous and non-equilibrium chemistry, three-dimensional modeling, and full characterization of rocket exhaust plumes and afterburning.

In addition to incorporating environmental considerations on an equal level with performance, cost, and reliability criteria from system conception to operation, potential avenues for consideration in future propulsion systems include formulation, testing, and demonstration of new and modified propellants, changing system operating parameters, modifying test facilities and protocols, and relocating test and launch facilities. However, it is essential to conduct detailed analyses of the costs, the benefits, and the risks of implementing such actions to ensure that safety and reliability are not compromised, that economics receive proper consideration, and that the actions taken do indeed reduce undesirable effects on the environment.

CONCLUSIONS AND RECOMMENDATIONS

(1) Global Nature of the Issues

CONCLUSION: Chemical rocket interaction with the environment has global implications and influence, requiring global understanding and mitigation strategies.

RECOMMENDATION: International cooperation should be developed to support and implement pertinent research and modeling, experiments, criteria formulation, development of monitoring instrumentation, and establishment of a common database. All nations which launch rocket-powered vehicles should contribute to the effort needed to gain an understanding of their interactions with the environment and their long-term effects. In addition, standards should be developed and accepted, where possible, by all pertinent nations. A mechanism should be created to fund this research on a joint international basis and share the results.

(2) Regulatory Implications

CONCLUSION: The principal effects of current and projected regulations on chemical rocket propulsion activities are likely to be as follows:

(a) International protocols. There will be an increasing array of restrictions designed to mitigate environmental impacts of launch vehicle testing and operations.

(b) Federal regulations. Certain propellants produce combustion products that are or will be regulated.

(c) State and local ordinances. State and local regulations begin with the federal rules as a minimum, and will probably be even more stringent.

RECOMMENDATIONS: (a) Integrate environmental factors at the conceptual stage of all rocket engine development programs, and evaluate propulsion alternatives in the light of their environmental impacts as well as traditional elements such as performance, cost, reliability, and operability.

(b) Conduct detailed cost-benefit trade studies of pathways for reducing environmental impacts of both current and projected chemical rocket systems without compromising reliability and safety. These studies should evaluate the principal contributors to environmental pollution in terms of the reduction obtained vs their cost of implementation.

(3) Scope of Atmospheric Environmental Effects

CONCLUSIONS: (a) Local environmental effects are caused by effluents containing acids, halogens, particulates, trace organics, and trace metals. Understanding of these effects; that is, in scientific and operational modeling, field and laboratory measurements and monitoring, acute and cumulative toxicology, wet and dry acid deposition, wetland and aquatic biosphere impacts, and opacity, is necessary for consideration of operational constraints.

(b) Models for analyzing and predicting effects of chemical rocket propulsion on the free troposphere involve regional and long-range transport, photochemistry, heterogeneous cloud processing, and cloud nucleation. One element not included in these models is the effects of exhaust particles on cloud formation.

(c) Models used to determine the stratospheric effects of rocket propulsion (e.g., ozone depletion and climate modification) are limited to 2-dimensional rather than 3-dimensional formulation and to homogeneous chemistry. Also, most rocket modeling studies include chlorine chemistry only.

(d) Computational models of the processes by which NOx is formed in the hot exhaust exist, but are not used to calculate NOx deposition rates.

(e) Understanding of the effect of particulates is not yet adequate for effective modeling.

RECOMMENDATION: Plan, initiate, and fund international research programs to:

(a) Formulate and implement heterogeneous models (initially two-dimensional, then three-dimensional) to determine stratospheric effects of chemical rocket propulsion.

(b) Establish accurate estimates of the NOx production by current and projected chemical rocket engines.

(c) Quantify the atmospheric interactions, including ozone-depleting potential, for the various exhaust products as a function of altitude.

(d) Conduct model calculations, both local and global, which include all major exhaust species and account for photochemical and other heterogeneous atmospheric reactions.

(e) Characterize effluent particulates (aluminum oxide, soot, ice, etc.), including their size distribution, shape, particle density, chemistry, etc. and estimates of their residence times in the atmosphere. Determine their effects on the background stratospheric aerosol content, on cloud formation, and

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on stratospheric ozone. Conduct laboratory measurements of the reactions of stratospheric constituents with aluminum oxide particulates.

(f) Develop analytical models for the formation of solid-particle products of combustion and for the solidification of ice particles during expansion that will enable the characterization of particulate quantity, size, shape, and number density during all launch and test phases.

(g) Use existing analytical models for rocket combustion, including mixing and burning with atmospheric gases (afterburning), not only for performance evaluation, as has been done in the past, but also to quantify the deposition of exhaust products in the atmosphere. Develop instrumentation and conduct experiments to generate appropriate anchoring data.

(h) Conduct model calculations, both local and global, which investigate influences on the mesosphere and ionosphere.

(i) Clarify the environmental interactions of the effluents of the different propellant combinations to identify the tradeoffs among halogens, the different particulates, trace organics and trace metals.

(4) Magnitude of the Effects

CONCLUSION: The general areas of concern in the effects of chemical rockets on the atmosphere are stratospheric ozone depletion, acid rain contributions, toxicity and air quality effects, and global warming. Based on the best available data and models, analyses performed in the U.S., Europe, and the Soviet Union were used to estimate the following effects of nine Shuttle and six Titan launches per year:

(a) On a global basis, the stratospheric ozone depletion from the deposition of chlorides ranges from 0.0065% to 0.024%. However, depletion is significantly higher in the northern mid-latitudes, where most Shuttle and Titan launches take place; that is, 9 Shuttle and 6 Titan launches annually produce about 2% of the inorganic chlorine formed from all anthropogenic sources in this region. Recent studies indicate that in the near vicinity of the plume during ascent, ozone depletion may be high (>80%) but returns to near normal levels rapidly (2 - 3 hours). Global ozone depletion due to heterogeneous reactions that take place on the surface of particulate Al_2O_3, soot, or water is expected to be small if the chemistry associated with rocket particulates is the same as that of natural stratospheric particulates. However, much remains unknown about the surface chemistry involved and about the interaction of chlorine with natural particles in the stratosphere.

(b) The global contribution to acid rain by chemical rockets is estimated to be less than 0.01%. Locally the effects are

strongly dependent upon a variety of factors. Current data suggest that the effects are confined to areas less than 2,500 feet from the launch site, but local conditions may affect different areas in ways that are not yet well defined.

(c) The contribution of chemical rockets to global warming is probably minute. The amount of CO_2 deposited in the atmosphere by rockets is 4×10^{-5}% of all anthropogenic CO_2 and 5×10^{-7}% of total CO_2 production, including natural sources. Contributions to the greenhouse effect due to particulate Al_2O_3 are unknown. However, the total surface area of aluminum oxide particles deposited in the stratosphere by ten Space Shuttle launches is less than 0.1% of the normal background stratospheric aerosol layer.

(d) The extensive experience base of chemical rocket testing and operations has demonstrated that toxicity hazards and local air quality are manageable by proper operational controls. One potential unknown might be synergistic effects between alumina particles and HCl, which require further study.

RECOMMENDATION: Although it has been concluded that the global atmospheric impact of chemical rocket propulsion is small, improvements should be sought in quantifying the character and effect of the effluents and in devising cost-effective measures which reduce or eliminate environmental concerns, as follows:

(a) Devise and conduct a program of diagnostic studies in the stratosphere which samples both the plume and near-plume regions of a space booster. In-situ measurements should include, but not be limited to, ozone concentration, ozone depletion precursors, and relevant species; e.g., NOx, ClO, and Clx. Methodologies for retrieving and preserving effluent samples without disturbance for post-flight laboratory analysis should also be developed and implemented.

(b) Quantify the effluent combustion products. Current definitions assume that reactions reach equilibrium conditions. However, combustion gases do not reach equilibrium in the nozzle. Test data are also needed to verify the nonequilibrium analytical models. The verified models should then be used to formulate improved propellants.

(c) Establish a program of in-situ testing, to define the physical and chemical composition of the effluent as a function of propellant formulation, altitude, temperature, and mixing processes. Conduct laboratory experiments to examine the effects of temperature, pressure, and particulates on ozone depletion kinetics. The program should include the design and development of instrumentation and test methods that can accurately define concentration levels of the chemical species, and should provide for real-time analysis capability.

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(5) **Rocket Engines and Motors**

CONCLUSIONS: (a) Although small compared with other anthropogenic effects, there are impacts on the environment due to rocket propulsion. The magnitude of these impacts is subject to debate, but technical experts agree unanimously that there are promising development options available to reduce the impacts as they are currently defined.

(b) A number of potential propellant-related pathways to reduced environmental impact have been identified. For solid propellants these include reduced-acid propellants, scavenged propellant, neutralized propellant, chlorine-free propellants, high-energy propellants, and hybrid rockets. For liquid propellants the options include propellant changes and mixture-ratio tailoring.

(c) It is imperative that actions taken to reduce emissions not reduce performance to the extent that additional launches would be required, which would negate the desired result of reducing pollutants. Reducing emissions of existing engines would require costly new engine development and recertification. Both these activities would require extensive test programs which would again negate the desired result of reducing pollutants. Hence the implementation of emission-reduction technology is likely to be practical only for new engines, not existing ones.

RECOMMENDATIONS: (a) Explore the various pathways to reduced environmental impact for next-generation rocket engines and motors (see above) by laboratory experiments and subscale testing.

(b) Conduct the analytical and experimental research needed to understand the environmental trades among particulates, chlorine compounds, CO, and CO_2 and develop a clear definition of what constitutes a minimum-impact solid propellant. Use the results of this research to continue and enlarge the current technology efforts to develop clean solid propellants and to identify and bring to operational readiness the most promising hybrid rocket concept.

(c) Evaluate the benefits of modifying liquid-propellant mixture ratios to reduce the level of hydrogen in the exhaust.

(d) Negotiate changing test protocols when environmentally sensitive propellants are involved; e.g., reducing test time for both engine development and engine acceptance.

(e) Evaluate the relocation of test facilities to areas where environmental impact will not be serious, to determine whether the benefits warrant the costs.

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I. INTRODUCTION

A. Purpose

The goals of this workshop were to identify and define the key environmental issues that relate to the effects on the atmosphere of rocket propulsion testing and use, to summarize what is known about them, and to recommend plans to address and resolve them through appropriate research.

It was recognized that rocket propulsion also involves manufacturing and disposal, and that the potential environmental effects of rocket propulsion are not limited solely to the atmosphere. However, it was decided that these aspects involve different technical disciplines and should therefore be considered separately in one or more subsequent workshops.

B. Workshop Genesis

In November 1990 the AIAA Propulsion and Energy Group and the Solid and Liquid Propulsion Industry Action Groups recognized the need to assemble factual information on the environmental effects of chemical propulsion of aerospace vehicles. Initial considerations included the effects of manufacturing, testing, and operating solid-propellant rockets, liquid-propellant rockets, and airbreathing engines (including the disposal of unused propellants) on the atmosphere, local terrain, the water table, etc. Specific atmospheric concerns included potential contributions to ozone depletion, air quality and toxicity, acid rain, and global warming.

Representatives of the two industry groups and various AIAA Technical Committees were invited to a preliminary meeting held

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in Reno, Nevada on January 11, 1991. At that meeting it was concluded that the aerospace profession, the space industry, and concerned environmental groups would benefit from a peer review of the available data aimed at defining approaches to better understand and further reduce environmental effects of chemical propulsion. It was decided to conduct a workshop to define more accurately the nature of the environmental concerns associated with chemical aerospace propulsion and to recommend actions aimed at understanding these concerns and reducing their impact.

The workshop program was initiated under the auspices of the AIAA Technical Services Department. A Steering Committee was appointed (see Appendix A-1) to serve as the program's "Board of Directors." At its first meeting (March 21, 1991) the Steering Committee decided to limit the scope of the workshop to the effects on the atmosphere (troposphere and stratosphere) of chemical-rocket testing and operations. The rationale for this decision was that manufacturing processes, propellant disposal, and environmental effects on local terrain and the water table all involve different technical disciplines and should therefore be dealt with by different groups of specialists at one or more subsequent workshops. Airbreathing propulsion was excluded because activities have been underway for several years studying the effects of effluents from airbreathing propulsion on the atmosphere.

The Steering Committee developed a list of candidates for participation, and those who accepted the AIAA's invitation and attended the workshop are listed in Appendix A-2. The workshop was held in Sacramento, California, on June 28-29, 1991,

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following the 27th Joint Propulsion Conference. The workshop agenda appears in Appendix A-3.

II. BACKGROUND

During the past year much press attention[1,2,3] has been directed at the environmental consequences to the atmosphere of testing and launching large rockets that utilize chemical propellants. Current scientific evaluations of the atmospheric impact of chemical propulsion[4-10] indicate that such impacts are confined or are very small relative to those of other causes, but questions still remain on the nature and the extent of these consequences.

Launch vehicles use both liquid and solid propellants. Virtually all current solid propellants consist of ammonium perchlorate (the oxidizer) and a polymer matrix containing powdered aluminum (the fuel). The common liquid propellant combinations are liquid oxygen and liquid hydrogen, liquid oxygen and liquid hydrocarbon fuels, and nitrogen tetroxide used with various hydrazine-based fuels.

On a single-launch basis, the Space Shuttle injects more exhaust products into the atmosphere than any other space launch system. The exhaust species generated by a single Shuttle launch and, equally important, where they are deposited in the atmosphere, are described in Table 1.

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TABLE 1

Effluents from a Single U.S. Space Shuttle Launch
(Thousands of Pounds, Rounded)

Species	Boosters (Solids)	Main Engines (Liquids)		
		0-15 km	15-50 km	>50 km
Water	500	240	180	1,000
Hydrogen	50	8	6	38
Hydrogen Chloride	500			
Aluminum Oxide	720			
Nitrogen	200			
Carbon Monoxide	65			
Carbon Dioxide	800			
Nitric Oxide	35			
Chlorine	20			
Iron Chloride	10			

III. CHEMICAL ROCKET SYSTEMS FOR LAUNCH VEHICLES

The chemical rocket propulsion systems used for launch vehicles in most countries employ a combination of liquid and solid propulsion subsystems. This circumstance evolved when the payload capabilities of launch vehicles initially powered by liquid-propellant rockets were augmented with solid-propellant boosters.

The characteristics of the chemical propulsion systems for the major international vehicles (see Figure 1) are presented in Table 2. The projected launch rates, current and future, appear in Table 3, broken down by country, launch site and launch rate. The table does not include launch rates of sounding rockets, tactical and strategic missiles, etc., since it is not possible to predict their launch rates, but their effluent contribution to the environment is negligibly small compared to that of the major launch vehicles.

Table 4 lists the exhaust quantities per launch for each

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Launch Vehicles Overview

China

Vehicle	Long March 1D	Long March-2C	Long March 4	Long March-3	Long March-3A	Long March 2E	Long March-2E/HO
First Flight	~1991	1975	1988	1984	~1992	1990	~1995
Performance LEO lb (kg)	1 650 (750)	7 040 (3 200)	8 800 (4 000)	11 000 (5 000)	15 800 (7 200)	20 430 (9,265)	29 900 (13 600)
GTO lb (kg)	440 (200)	2 200 (1 000) + PKM	2 430 (1 100)	3 300 (1 500)	5 500 (2 500)	7 430 (3 370) + PKM	9 900 (4 500)
Launch Site	• Juquan	• Juquan	• Tayuan	• Xichang	• Xichang	• Xichang	• Xichang

Vehicle	Ariane 40	Ariane 42P
First Flight	1990	1990
LEO lb (kg)	10 800 (4 900)	13 400 (6 100)
GTO lb (kg)	4 190 (1 900)	5 730 (2 600)
Launch Site	• Kourou	• Kourou

Israel

Vehicle	Shavit
First Flight	~1988
LEO lb (kg)	350 (160)
GTO lb (kg)	—
Launch Site	• Negev

Japan

Vehicle	M-3S II	M V	H 1	H-2
First Flight	1985	~1995	1986	~1993
LEO lb (kg)	1 720 (1 815)	4 300 (1 950)	7 000 (3 200)	23 000 (10 500)
GTO lb (kg)	1 140 (517) + PKM	2 680 (1 215) + PKM	2 400 (1 100)	8 800 (4 000)
Launch Site	• Kagoshima	• Kagoshima	• Tanegashima	• Tanegashima

(United States)

Vehicle	SCOUT	Enhanced SCOUT	Pegasus	Taurus	Delta II 6925
First Flight	1979	—	1990	~1992	1989
LEO lb (kg)	600 (270)	1 160 (525)	1 000 (455)	3 200 (1 450)	8 780 (3 990)(3)
GTO lb (kg)	120 (54)	240 (110)	275 (125) + PKM	830 (375)	3 190 (1 450)
Launch Site	• Wallops • Vandenberg • San Marco	• Wallops • Vandenberg • San Marco	• B 52 aircraft	• Vandenberg	• Cape Canaveral • Vandenberg

Soviet Union

Vehicle	Kosmos (C 1 SL 8)	— (F 1 m / SL 11)	Tsyklon (F 2 SL 14)	Vostok (A-1 SL 3)	Molniya (A 2-e / SL-6)	Soyuz (A-2 SL 4)	Zenit 2 (J 1 SL 16)	Zenit 3 (J 1 SL 16)	Proton (D 1-e SL 12)	Proton (D 1 SL 13)
First Flight	~1964	~1967	~1977	~1959	1961	~1963	1985	~1993	1967	~1968
LEO lb (kg)	3 000 (1 350)	—	8 800 (4 000)	10 400 (4 730)	—	15 400 (7 000)	30 300 (13 740)(1)	—	—	44 100 (20 000)
GTO lb (kg)	—	—	—	—	3 300 (1 500) Molniya	—	—	9 480 (4 300)(1)	12 100 (5 500)	—
Launch Site	• Plesetsk • Kapustin Yar	• Tyuratam	• Plesetsk	• Tyuratam	• Tyuratam • Plesetsk	• Tyuratam • Plesetsk	• Tyuratam	• Tyuratam	• Tyuratam	• Tyuratam

FIGURE 1

Ariane 44P	Ariane 42L	Ariane 44LP	Ariane 44L	Ariane 5	Ariane 5 / Hermes	SLV-3	ASLV	PSLV	GSLV [2]
—	—	1988	1989	~1995	~1998	1979	1987	~1991-92	~1995-96
~5 200 (6 900) 6 610 (3 000)	16 100 (7 400) 7 050 (3 200)	18 300 (8 300) 8 160 (3 700)	21 100 (9 600) 9 260 (4 200)	39 600 (18 000) ~5 000 (6 800)	6 600 (3 000)	90 (40) —	330 (150) —	6 600 (3 000) 990 (450)	17 600 (8 000) 5 500 (2 500)
· Kourou	· Kourou	· Kourou	· Kourou	· Kourou	· Kourou	· Sriharikota	· Sriharikota	· Sriharikota	· Sriharikota

United States

Delta II 7925	Atlas E	Atlas I	Atlas II	Atlas IIA	Atlas IIAS	Titan II SLV	Titan III	Titan IV	Space Shuttle
1990	1974	1990	~1991	~1991	~1993	1988	1989	1989	1981
11 100 (5 045) [3] 4 010 (1 820)	1 800 (820) Polar —	12 300 (5 580) 4 950 (2 250)	14 100 (6 395) 5 900 (2 680)	14 900 (6 760) 6 200 (2 810)	18 500 (8 390) 7 700 (3 490)	4 200 (1 905) Polar [4] —	32 000 (14 515) 11 000 (5 000)+PKM	39 000 (17 700) [5] 10 000 (4 540) GEO [6]	53 700 (24 400) [7] 13 000 (5 900) + PKM
· Cape Canaveral · Vandenberg	· Vandenberg	· Cape Canaveral	· Cape Canaveral	· Cape Canaveral	· Cape Canaveral	· Vandenberg	· Cape Canaveral	· Cape Canaveral · Vandenberg	· Kennedy Space Center

Launch Sites

Plesetsk (62 8°N)
Kapustin Yar (48 4°N)
Jiuquan (40 7°N)
Tyuratam (45 6°N)
Taiyuan (?°N)
Kagoshima (31 2°N)
Tanegashima (30 2°N)
Xichang (28 2°N)
Wallops (37 9°N)
Vandenberg (34 7°N)
Canaveral (28 5°N)
Negev (~31°N)
Sriharikota (13 9°N)
Kourou (5 2°N)
Equator
San Marco (2 9°S)

Energia (K 1 SL 17)	Energia / Buran (K 1 SL 17)
1987	1988
94 000 (88 000) [?] 40 000 (18 000) GEO [?]	66 000 (30 000) —
· Tyuratam	· Tyuratam

Notes
[1] LEO low Earth orbit
GTO geosynchronous transfer orbit
GEO geosynchronous orbit
PKM perigee kick motor
[2] Configuration is being finalized
[3] LEO version is designated 6920 or 7920
[4] Plus 53% Polar with 10 solid strap ons
[5] Plus 25% LEO with SRMU
[6] With Centaur upper stage
[7] Plus 10-20% LEO with ASRM
[8] Plus 15% LEO from Cape York
[9] Plus 35% GTO from Cape York
[10] With RCS kick stage
[11] With EUS upper stage

AIAA

International Reference Guide to Space Launch Systems

FIGURE 1 (continued)

TABLE 2

CHARACTERISTICS OF PROPULSION SYSTEMS FOR MAJOR SPACE LAUNCH VEHICLES

COUNTRY	APPLICATION	ENGINE/MOTOR	VACUUM THRUST (lbf)	PROPELLANT COMBINATION	EXHAUST PRODUCTS
China	Long March	YF-73	9,900	O_2/H_2	H_2, H_2O
Europe	Ariane 4	HM7	14,000		
	Ariane 5	Vulcain	242,000		
USA	Centaur	RL10A-3-3A	16,500		
	STS	SSME	470,000		
	ALS, NLS	STME	580,000		
Japan	H-1, H-2	LE-5	25,000		
	H-2	LE-7	265,000		
USSR	Energia	RD-0120	441,000		
USA	Atlas	MA-5A Sustainer	84,400	$O_2/RP-1$	CO, CO_2, H_2, H_2O
		MA-5A	469,200		
		RS-27A	237,000		
Japan	Delta	MB-3	172,500		
USSR	N-2, H-1	RD-?	19,000		
	Proton	RD-170	444,200		
	Energia				
China	Long March	YF-22	162,000	N_2O_4/Hydrazine (Aerozine 50)	CO, CO_2, H_2, H_2O, N_2, NOx
Europe	Ariane	Viking	170,000		
USA	Titan, Delta	AJ10-118	9,700		
	N-2 (Japan)				
	Titan	LR-91	100,000		
	Titan	LR-87	548,000		
USSR	Proton	RD-?	135,000		
	Proton	RD-253	368,000		
Europe	Ariane 4	P9.5	146,000	Solid	HCl, Al_2O_3, CO_2, CO, N_2, H_2, H_2O
	Ariane 5	EAP/MPS	1,433,000		

Country	Vehicle	Motor	Thrust
USA	STS		3,000,000
		RSRM	
		ASRM	
	Titan 34D	UA 1205	1,000,000
	Titan IV	UA 1207	1,200,000
	Titan II	Castor	1,122,410
	Atlas IIAS	Castor 4A	394,000
	Delta 6920	Castor 4A	929,400
	Delta 7920	GEM	985,500
	N-2	Castor 2	468,000
	H-1A	Castor 2	468,000
	H-2	Nissan	46,200
	MU-3S-2	M-13	283,000
		SB-735	73,700
		M-23	117,500
		M-3B	29,700
Japan	M-5	M14	947,720
		M24	308,560
		M34	65,500

TABLE 3
PROJECTION OF LAUNCH RATES
FOR CHEMICAL ROCKET LAUNCH VEHICLES

COUNTRY	LAUNCH VEHICLE	LAUNCH SITE	YEARLY LAUNCH RATE - 1991	YEARLY LAUNCH RATE - 2000
China	Long March 2	Xichange	2.0	4 0
	Long March 3	Xichange	N/A	N/A
Europe	Ariane	Kourou	5.0	9.0
Japan	MU 35	Kogoshima	1.0	0.0
	N-2	Tanegashima	1.0	0.0
	H-1	Tanegashima	1.0	0.0
	H-2	Tanegashima	0.0	2 0
USA	Atlas	VAFB, KSC	4 0	8 0
	Delta	VAFB, KSC	5 0	8.0
	STS	KSC	6 0	10 0
	Titan	VAFB, KSC	4 0	10.0
USSR	Soyuz	Baikonur	38.0	
	Tsyklon	Baikonur	14.0	
	Cosmos	Baikonur	10.0	
	Proton	Baikonur	11.0	
	Molniya	Baikonur	9.0	50
	Zenit	Baikonur	2.0	
	Vostok	Baikonur	1.0	
	Energia		1 0	

launch vehicle. Some of the data in Table 4 are based on theoretical calculations using the CET89 code; some are derived from References 11-17. In some cases effluent data were not available, so the effluents of those launch vehicles were estimated assuming that they could be approximated by the exhaust quantities of "equivalent" U.S. launch vehicles. Table 4 breaks down the data by launch vehicle, exhaust product, weight per flight as a function of altitude, and total quantity of effluents in the exhaust.

IV. SOLID-PROPELLANT ROCKETS

A. Introduction

In a solid-propellant rocket motor the fuel and oxidizer, whose combustion sustains the high chamber pressures required to develop thrust, are premixed and allowed to solidify inside the combustion chamber. The casting process is controlled so that the propellant "grain" forms into the proper shape for the desired thrust-vs-time profile, and proper insulators and inhibitors are used to protect the thrust-chamber casing and control the combustion process. These physical constraints impose limitations on propellant performance (i.e., specific impulse), effluent composition, and operational flexibility; that is, once ignited, the thrust schedule cannot be varied or terminated without destroying the rocket motor. The primary benefits of solid-propellant rockets are their high density (reducing launch-vehicle size), reliability, low cost, long-term storability, and immediate availability for launch and flight when needed. These

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TABLE 4
EXHAUST QUANTITIES PER LAUNCH VEHICLE

Launch Vehicle	Exhaust Product	Weight Per Flight (lbm)			Total Weight (lbm)
		0-15km	16-50km	>50km	
Atlas II (USA)	CO	64,410	38,120	10,230	112,760
	CO_2	52,850	31,370	9,510	93,730
	H_2	2,450	1,430	2,670	6,550
	H_2O	63,020	36,100	40,960	140,080
Atlas II, AS (USA)	CO				128,710
	CO_2				95,840
	H_2				8,130
	H_2O				146,260
	HCl				13,980
	N_2				5,500
	OH				20
	H				20
	Al_2O_3				20,000
STS (USA)	H_2 (SSME)	8,490	6,410	38,240	53,140
	H_2O (SSME)	241,220	182,200	1,086,590	1,510,010
	CO (Total)				574,560
	CO_2 (Total)				84,240
	H_2 (Total)				102,880
	H_2O (Total)				1,735,360
	N_2 (Total)				208,800
	HCL (Total)				502,560
	OH (Total)				720
	H (Total)				720
	Al_2O_3 (Total)				720,000
Delta II (USA)	CO (Liquid)	20,360	20,690	48,320	89,370
	CO_2 (Liquid)	15,380	15,620	40,240	71,240
	H_2 (Liquid)	730	740	1,950	3,420
	H_2O (Liquid)	12,340	12,540	31,420	56,300
	N_2 (Liquid)			4,410	4,710
	CO (Total)				125,160
	CO_2 (Total)				76,515
	H2 (Total)				6,605
	H2O (Total)				70,335
	N2 (Total)				17,800
	HCl (Total)				31,455
	OH (Total)				45
	H (Total)				45
	Al_2O_3				45,000
Titan IV (USA)	CO (Liquid)		2,280	18,550	20,830
	CO_2 (Liquid)		7,400	64,940	72,340
	H_2 (Liquid)		270	2,630	2,900
	H_2O (Liquid)		15,000	125,420	140,420
	N_2		18,800	160,120	178,920
	CO (Total)				284,140
	CO2 (Total)				110,010

	H_2 (Total)	25,778
	H_2O (Total)	243,690
	N_2 (Total)	276,700
	HCl (Total)	230,670
	OH (Total)	330
	H (Total)	330
	Al_2O_3	330,000
Anane 5	CO (Liquid)	3,459
(Europe)	CO_2 (Liquid)	12,041
	H_2 (Liquid)	3,637
	H_2O (Liquid)	117,305
	N_2 (Liquid)	29,771
	CO (Total)	231,767
	CO_2 (Total)	45,515
	H_2 (Total)	23,376
	H_2O (Total)	202,854
	N_2 (Total)	112,740
	HCl (Total)	119,984
	OH (Total)	286
	H (Total)	286
	Al_2O_3	286,100
Energia	CO	1,242,940
(USSR)	CO_2	863,052
	H_2	107,992
	H_2O	2,635,292
	H	924
Zenit (USSR)	CO	1,566,104
	CO_2	1,087,446
	H_2	52,280
	H_2O	945,956
	H	1,164
Long March	CO	26,832
(China)	CO_2	93,396
	H_2	3,612
	H_2O	181,116
	N_2	230,910
H-2 (Japan)	H_2 (Liquid)	5,796
	H_2O	164,509
	CO (Total)	106,740
	CO_2 (Total)	15,650
	H_2 (Total)	15,025
	H_2O (Total)	206,376
	N_2 (Total)	3,879
	HCl (Total)	93,498
	OH (Total)	134
	H (Total)	134
	Al_2O_3 (Total)	133,760

features have made solid-propellant rockets the desired choice for most weapon systems. Large solid-rocket boosters (SRBs) also produce over 80% of the Shuttle's boost-phase thrust.

Solid-propellant rockets that launch military weapons, particularly large ballistic missiles (ICBM, IRBM, and SLBM), are also tested frequently by both the U.S. and the Soviet Union. The effluents from these tests, which in the U.S. are conducted about once per month, are included in the atmospheric impact assessment. The effluents produced from each such launch average about __% of those due to a Shuttle launch.

The largest solid-propellant rockets flown are those employed on NASA's Space Shuttle and the Titan-4 Air Force launcher. Smaller solid-propellant rockets are used for thrust augmentation at launch on the Delta and Delta-2, the Atlas-2AS, and several Ariane-4 configurations, as well as on Chinese Long March (CZ-2) and Japan's forthcoming (1993) H-2. The Ariane-5, to begin flying around 1995, will employ large boosters somewhat smaller than Titan-4's. Several smaller space launchers employ all-solid propulsion systems; e.g., the U.S. Scout, Pegasus. Taurus, and Conestoga, Japan's Mu-series, India's SLV and PSLV, and Israel's Shavit.

Current and projected solid-rocket boosters for the two largest launchers, the Shuttle and Titan-4, use ammonium perchlorate oxidizer and a polymer fuel (the propellant binder) loaded with powdered aluminum. The principal effluent of interest are hydrogen chloride (HCl), aluminum oxide (Al_2O_3), water (H_2O), hydrogen (H_2), carbon monoxide (CO) and carbon dioxide (CO_2). Total depositions per Shuttle launch were given

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previously in Table 1. Current projections for annual Shuttle launch rate range from six to ten per year, depending in part on the resolution of Space Station Freedom manifests. The Air Force recently projected Titan-4 launches at an average of about four per year. Ariane-5's launch frequency has not yet been established, but should peak at no more than nine per year around 2000. The most probable successor to the Shuttle, the National Launch System (NLS), will use a solid booster similar to that employed on the current Shuttle, but is planned to be launched less frequently than the Shuttle. The final configuration of the Air Force version of the NLS that is being considered to succeed Titan-4 has not yet been defined, except that its core and that of NASA's vehicle will use a common liquid propulsion system. Projected annual depositions of all major solid-propellant launch motors for the year 2000 appear in Table 5.

Current public attention on the atmospheric environmental effects of space launch vehicles employing solid-propellant rockets is focused on four areas: stratospheric ozone depletion; acid rain; toxicity; and global warming. Section VI of this report summarizes what is currently known about these effects and where further work is needed to better understand future impacts of rocket launches.

It is also extremely important to evaluate the cost/benefit trades of making future rocket systems more environmentally benign without compromising the reliability and safety that are essential for space launch propulsion systems.

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TABLE 5
ANNUAL EXHAUST QUANTITIES FOR
SOLID PROPULSION MOTORS
OF ALL LAUNCH VEHICLES PROJECTED FOR YEAR 2000

LAUNCH VEHICLE	EXHAUST PRODUCTS	TONS/YR
Atlas II-AS (based on 8 launches per year)	CO	63
	CO_2	9
	H_2	6
	H_2O	25
	N_2	23
	HCl	56
	OH	0 1
	H	0.1
	Al_2O_3	80
Delta II (based on 8 launches per year)	CO	144
	CO_2	21
	H_2	12
	H_2O	56
	N_2	52
	HCl	126
	OH	C 2
	H	0 2
	Al_2O_3	180
STS (based on 10 launches per year)	CO	2,673
	CO_2	421
	H_2	248
	H_2O	1,127
	N_2	1,044
	HCl	2,513
	OH	3.6
	H	3 6
	Al_2O_3	3,600
Titan IV (based on 10 launches per year)	CO	1,317
	CO_2	193
	H_2	115
	H_2O	516
	N_2	489
	HCl	1,153
	OH	1 7
	H	1 7
	Al_2O_3	1,650

B. Pathways for Further Reduction of Emissions

Although the impact of solid-propellant rocket motors is currently estimated to be small, the solid-propellant rocket community has identified options that could further reduce these impacts. The options fall into two basic categories: alternative solid propellants and hybrid rockets.

Currently identified solid-propellant options have focused on the reduction of hydrogen chloride (HCl). These potential alternatives and their effects are shown in Table 6. Most of the options appearing in Table 6 are in the very early stages of development; cost-benefit analyses of their implementation in current or future launch systems have not yet been performed.

Hybrid rockets typically use one ingredient in liquid form and one as a solid. These rockets therefore exhibit features of both solid-propellant and liquid-propellant systems, as well as some unique features of their own. They offer potential benefits in both design and operation. All hybrids currently under development utilize a liquid oxidizer and a solid fuel, typically liquid oxygen and polybutadiene fuel. The projected performance of these propellants is almost identical to that of the liquid oxygen/RP-1 combination used in the Delta and Atlas launch vehicles.

The emissions from a hybrid using this propellant combination are similar to those of a liquid oxygen/RP-1 engine; primarily water, carbon dioxide, carbon monoxide and hydrogen, as shown in Table 7. Other propellant combinations are possible; most do not produce either HCl or Al_2O_3. The net result is

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potentially reduced environmental impact.

Hybrids are not currently used for space launch vehicles, but are currently in the early stages of development in the U.S., Europe, and Israel.

TABLE 7
Exhaust Emissions from Typical Liquid, Hybrid, Solid Rocket Motors
(lbm/sec per 100,000 lb thrust)*

Species	$LO_2/RP-1$	Hybrid	Solid
H_2O	81.1	64.1	31.3
CO_2	93.6	103.9	11.7
CO	134.8	137.0	79.8
HCl			69.9
Al_2O_3			100.0
H_2	4.5	3.0	6.9
H	0.1	0.0	0.1
OH	0.0	0.1	0.1
N_2		1.2	29.0

*Theoretical calculations using CET89 code

V. LIQUID-PROPELLANT ROCKETS

A. Liquid-Propellant Rocket Systems

Liquid propellants are used for the main propulsion of all international space launch vehicles. Many of these are thrust-augmented by solid propellant boosters. The three liquid propellant combinations currently in use are liquid oxygen/hydrocarbon, nitrogen tetroxide/"Aerozine" (a mixture of unsymmetrical dimethylhydrazine and hydrazine), and liquid oxygen/liquid hydrogen.

Some spacecraft use attitude control systems employing the monopropellant hydrazine or the bipropellant combination nitrogen

tetroxide/monomethylhydrazine (MMH). These engines require ground testing and create products of combustion similar to those of main propulsion systems using these propellants. Effluent quantities from such tests, as well as those released from use of attitude control systems during spaceflight, are negligibly small.

Each propellant combination has its own unique properties that determined its choice for specific launch-vehicle characteristics. Table 8 summarizes those properties.

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Table 8. Propellant Characteristics

PROPELLANTS Fuel	PROPELLANTS Oxidizer	TYPICAL VACUUM Specific Impulse* (sec.)	TYPICAL Bulk Density (lbm/ft)	STORAGE TEMP. Fuel	STORAGE TEMP. Oxidizer (F)
Kerosene (RP-1)	Liquid Oxygen	295	63	AMB	-295
Aerozine	Nitrogen Tetroxide	270	70	AMB	AMB
Liquid Hydrogen	Liquid Oxygen	440	23	-420	-295
Hydrazine (Monopropellant)		230	63	AMB	

The combination of kerosene and liquid oxygen was selected for use in the launch vehicles that started the space programs of most countries. Its good performance (specific impulse) and high density allowed the use of minimum-size launch vehicles. The low cost and ambient storage temperature of kerosene make it suitable as a rocket fuel. The use of liquid oxygen/kerosene over many years has resulted in high vehicle reliability, an excellent safety record, and efficient launch operations.

The Aerozine/nitrogen tetroxide propellant combination offers hypergolic, ambient-temperature-storable propellant, but at a specific impulse somewhat lower than propellant combinations using liquid oxygen. Their long-term storability is important for spacecraft attitude control systems, some of which must function frequently over a period of more than ten years. The Titan launch vehicle was originally developed as a military ballistic missile, and therefore required storable propellants to make it available for launch at any time. Unsymmetrical dimethyl

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hydrazine (UDMH) was added to hydrazine (N_2H_4), forming Aerozine 50, to make it suitable for stable combustion in large rocket engines. The Titan vehicle continues to serve as an important launch vehicle.

Liquid hydrogen and liquid oxygen deliver the greatest specific impulse of all propellants used in launch vehicles, resulting in the lowest launch mass. The very low temperature of hydrogen and its very high combustion temperature (with oxygen) precluded its early use in the space program; technology advancements enabled its use in the upper stages of the Apollo program's Saturn V rocket, and it was subsequently used in the space shuttle main engine (SSME).

With a solid-particle catalyst bed, hydrazine is used as a monopropellant in spacecraft attitude control systems. Its storability and high reliability make it attractive for this purpose. However, its lower specific impulse requires more propellant than bipropellant combinations such as nitrogen tetroxide/MMH.

B. Exhaust Effluents

Projected launch rates were given earlier in Table 3, Section III. Note that although the Soviet launch rate is likely to decrease due to improvements in spacecraft lifetimes and reductions in overall space activities in the USSR, it is not likely to fall much below about 50 launches per year (all large vehicles), and hence will continue to dominate global emissions from liquid-propellant rockets.

For the future, there are two near-term new launch vehicles

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being considered: the National Launch System (NLS) and a rocket-powered reusable single-stage-to-orbit (SSTO) concept. Both use liquid hydrogen as fuel and liquid oxygen as oxidizer. The NLS family may also utilize solid-propellant boosters.

The equilibrium emissions from the three propellant combinations used in liquid-propellant rockets are listed in Table 9. The projected total release of exhaust products from liquid-propellant systems in the year 2000 appears in Table 10. Total annual emissions per launch vehicle appeared earlier in Table 4, Section III.

Table 9

Equilibrium Emissions from Liquid-Propellant Rockets
(Percent of Total Exhaust Products)

Product	N2O4/Aerozine-50	LO2/RP-1	LOX/LH2
CO	0.03561	0.35954	0
CO_2	0.09563	0.14479	0
H	0.00006	0	0
H_2	0.04969	0.26265	0.058
H_2O	0.45886	0.23301	0.942
OH	0.00003	0	0
N_2	0.35012	0	0

As the exhaust is discharged into the atmosphere, afterburning will occur, modifying the mole fractions and introducing some new compounds such as NOx, which are eventually deposited in the atmosphere. Quantitative data on the products generated by afterburning as a function of altitude are not

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TABLE 10
ANNUAL EXHAUST QUANTITIES FOR LIQUID PROPULSION ENGINES OF ALL LAUNCH VEHICLES PROJECTED FOR YEAR 2000
(Afterburning Not Included)

LAUNCH VEHICLE	EXHAUST PRODUCTS	TONS/YR 0-15km	TONS/YR 15-50km	TONS/YR >50km	TOTALS
Atlas II-AS	CO	258	152	41	451
(based on	CO_2	211	125	38	374
8 launches	H_2	10	6	11	27
per year)	H_2O	252	144	164	560
Delta II	CO	81	83	193	357
(based on	CO_2	62	62	161	285
8 launches	H_2	3	3	8	14
per year)	H_2O	49	50	126	225
	N_2	0	0	19	19
STS	H_2	42	32	192	266
(based on	H_2O	1,206	911	5,433	7,550
10 launches					
per year)					
Titan IV	CO	0	11	93	104
(based on	CO_2	0	37	325	362
10 launches	H_2	0	1	13	14
per year)	H_2O	0	75	627	702
	N_2	0	94	801	895
Anane 5	CO				15
(based on	CO_2				119
9 launches	H_2				16
per year)	H_2O				510
	N_2				134
H-2	H_2				6
(based on	H_2O				165
2 launches					
per year)					

currently available.

Ground-testing is performed on all liquid-propellant engines before integrating them into their launch vehicles. Appropriate controls are currently in place to minimize contamination of ground waters and soil by the cooling water used in these tests.

C. Issues

The major environmental contribution by liquid rockets to the troposphere occurs during static ground tests of rocket engines. During launch, the dwell time of effluents in the troposphere is relatively short -- only a few seconds -- depending on the launch vehicle. Indeed, in some launch vehicles, such as the Titan-IV, first-stage liquid engines are ignited above the troposphere. However, the engine ground-test duration may be the full mission burn time. The negative effects are limited to health risks associated with creation of ozone precursors, particulate emission, and trace levels of toxic products resulting from the propellant burning. The ozone precursors include NOx and CO/CO_2. In most cases the total NOx and CO emissions from rocket engine testing at a given location do not reach the levels of interest expressed in the 1990 Clean Air Act Amendments. The levels of toxicity associated with the products found in the rocket engine exhausts are extremely low and are mitigated by evacuation of test areas during the testing. No significant deposition of these trace levels of toxic materials occurs outside the test area.

The liquid-propellant rocket engine exhaust effects on the stratosphere occur during launch. Here the effluents of concern

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are primarily OH, H, and NOx, along with particulate ice and carbon. The reactions of the hot exhaust with the ambient air to form NOx, as well as subsequent reactions of the free hydrogen dispersed, need to be evaluated to ascertain accurately the quantitative scope of these effects. The quantity, shape, size distribution, and chemistry of particulates introduced into the stratosphere should also be evaluated.

D. Approaches to Controlling Emissions of Liquid Rocket Engines

Environmental concerns for emissions in the troposphere and stratosphere regimes are different. Emissions in both regimes depend on the physics and chemistry of the selected propellants. This imposes fundamental limits on the degree of control.

Emissions of concern are somewhat different for the three propellant combinations. These can be broken down into "primary" and "secondary" emissions. Primary emissions are produced directly by the engine itself; secondary emissions are products formed through interaction of the exhaust plume with the environment.

The primary emissions from the three liquid propellant combinations mentioned previously are shown in Table 11.

Table 11

Primary Emissions from Three Propellant Combinations

LO_2H_2	$LO_2/RP-1$	$N_2O_4/Aerozine$
H_2	H_2	H_2
H_2O	H_2O	H_2O
	CO_2	CO_2
	CO	CO
		N_2

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Hydrogen and water are common for all three, CO and CO_2 are common for two, and N_2 is released only by N_2O_4/Aerozine. In addition, all three can produce trace amounts of hydroxyl (OH) radicals. Particulate carbon (soot) can also be produced by LO_2/RP-1 and N_2O_4/Aerozine.

The impacts in the troposphere regime are short-term and local. There are no known adverse effects of hydrogen, water, carbon dioxide, or nitrogen for the total quantities exhausted. Both soot and CO are regulated for test stand operation.

Secondary emissions occur when hot exhaust gases interact with air to produce oxides of nitrogen (NOx). Nitrogen oxides are known participants in the formation of photochemical smog and acid rain. The quantities of this secondary emission of NOx are low and their significance is largely unknown.

Emissions in the stratosphere regime involve two areas of concern: global warming and ozone-layer depletion. Global warming results from blockage of Earth's radiation to space by gases that are opaque to infrared emission. CO_2, created by two of the propellant combinations, produces this effect.

As discussed earlier, depletion of the ozone layer results from catalytic reaction of ozone in the presence of certain pollutants. Since the reaction leaves the catalyst unchanged, the process can repeat as long as the catalytic molecule remains in the ozone layer. The OH radical, produced directly by rocket engines and by secondary reactions of rocket-generated water, is one such catalyst. Hydrogen molecules produced by the engine do not themselves react catalytically, but can be photochemically dissociated to hydrogen atoms, which catalyze ozone conversion to

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water vapor and free oxygen. Particulate emissions such as soot and ice crystals could also influence ozone depletion, and need to be studied. Based on recent studies[9] the effects due to secondary emissions of NOx in the stratosphere need to be evaluated.

The range of options for reducing emissions that affect the environment is limited and the potential reductions are small. These options must be carefully studied, because they could have negative impacts on performance, reliability, safety, and cost. For example, performance reductions could require additional launches to meet mission requirements, thereby increasing negative impacts on the environment. Environmental impacts should be considered in the design of future engines, but unless realistic international standards and regulations are established and accepted, competition will tend to stress traditional design elements such as performance, weight, reliability, and cost.

Some specific prospects for reducing the environmental impact of liquid propellant engines are:

o Consider environmental impacts on selecting future rocket engine design concepts.

o Modify mixture ratio to reduce the level of H_2 in the exhaust.

o Negotiate changes in test protocol for environmentally sensitive propellants, such as reduced test time for engine acceptance and reduced testing in development programs.

o Evaluate the relocation of test facilities to areas where environmental impact will not be serious, to determine if the benefits warrant the costs.

o Curtail use of the more harmful propellants.

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o Evaluate the costs and benefits of using enclosed test facilities equipped with exhaust scrubbers.

Potential improvements in new engine designs could provide some reduction in pollution and therefore deserve study. However, reducing emissions on existing engines would require extensive development programs, and therefore is likely to be expensive. Changes such as mixture-ratio modification or the curtailing of more harmful propellants in existing engines will require redevelopment and recertification, as well as create local environmental impacts due to the increased testing required to validate the modification. Hence careful cost-benefit analyses need to be conducted before proceeding with any of these options, as noted previously. The most effective approach would be to continue use of existing vehicles and apply promising emission-reduction technologies to new designs.

VI. CRITERIA FOR QUANTIFYING ATMOSPHERIC EFFECTS
A. Background

Predicting and understanding the environmental effects of testing and launching chemical rockets encompasses a complex array of issues which collectively define the "impact". For atmospheric impact, the effects can be divided into three distinct categories: (1) the lower troposphere under the boundary layer; (2) the upper troposphere above the boundary layer; and (3) the stratosphere. Within each of the atmospheric layers, eight categories of rocket exhaust products were identified, as listed in Table 12.

Numerical standards and guidelines are provided in federal,

TABLE 12
CHEMICAL ROCKET EXHAUST PRODUCTS

PRODUCT	SOURCE (EXAMPLE)	ROCKET TYPE
Halogens (acid)	Perchlorate	Solid
Metal particles	Aluminum	Solid
Soot particles	Kerosene	Liquid
CO and CO_2	Kerosene, solid binder	Solid, liquid, hybrid
NO_x	Atmospheric nitrogen (oxidation), hydrazine, nitrogen tetroxide	Solid, liquid, hybrid
H_2, H_2O, HO_x	LOX/LH2, LOX/RP-1, solid binder, hydrazine	Solid, liquid, hybrid
Trace metals	Burn-rate catalysts	Solid
Trace organics	Solid binder	Solid

state, and local environmental regulations. Further criteria are beginning to be formulated on an international level through multinational agreements such as the Montreal Protocol. In the future national and international laws will profoundly influence decisions on the use and choice of chemical rocket systems, as will economic considerations of launch activities. Where guidelines or standards are not exact or have not been established by law and impact has been recognized, a qualitative perspective is necessary, based on the information available.

Emphasis should be placed on understanding the cumulative impacts of future launch systems designed for high launch rates. Natural environments are resilient only to some degree. We cannot yet identify when the introduction of anthropogenic chemical releases that perturb the natural ecosystem reach the point at which the ecosystem cannot recover and harm is incurred. Current knowledge of impacts should be used to project maximum future impacts of new systems, and decisions on future propulsion system (especially high-rate-use systems) should be made by balancing the reduction of environmental impacts with technological risk factors. Collective impacts should be determined by considering all processes involved, from raw material to finished product and launch.

Guidelines to achieve acceptable environmental impact are as follows:

(1) Environmental laws and regulations provide threshold criteria for environmental impact.

(2) Absolute and integrated impact assessment provides the basis for environmentally responsible decisions on the

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development and operation of rocket propulsion systems.

(3) Relative impact assessment provides a perspective for quantification and characterization of the degree of environmental impact.

(4) The National Environmental Policy Act requirements and associated policies for early definition of environmental impact and evaluation of risk in the development of aerospace systems should be fully implemented.

(5) Research to define, understand, and minimize environmental impact should be an integral part of propulsion system research, development, and education.

(6) Continuous environmental measurement and analysis to determine, gauge, and monitor environmental impact should be integral to propulsion system testing and operation.

B. Regulations and Protocols

(1) The National Environmental Policy Act (NEPA)

(a) NEPA Process for New Launch Vehicle Programs

The NEPA process and consideration of environmental factors should be initiated early and become an integral part of the conceptual phase of new launch-vehicle programs. Such an approach will ensure that all reasonable alternatives and their environmental impacts are adequately considered. Committing resources early to initiate the NEPA process for a new rocket program would demonstrate that the parties involved are making sure environmental concerns are evaluated before design decisions are finalized.

(b) NEPA Process for Ongoing Rocket Programs

For ongoing rocket programs, the Council on Environmental Quality recommends that the existing underlying environmental documentation be reexamined periodically at five-year intervals. This ongoing reexamination process ensures that the program description and relevant environmental information is up-to-date

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and accurate. The end product would be an environmentally responsible document that would be published and available to all interested parties. This document would then lay the framework for further study of areas that may be sensitive to changing environmental regulations.

(c) Clean Air Act Amendments

The Clean Air Act Amendments (CAAA) of 1990 dramatically expanded the scope and stringency of U.S. air pollution control laws. Managers of rocket programs must be aware of the implications of these legal requirements and take them into account in planning and conducting their activities. Consideration should be given to the fact that the combustion products of certain propellants may be regulated under the Clean Air Act. Balancing the impact of these legal procedures and air quality requirements with other relevant design and implementation factors may well affect the nature of the propellant used and the design and implementation of the testing program.

The prevention of significant deterioration and nonattainment provisions of the CAAA for stationary sources may be triggered for any rocket motor/engine testing which generates nitrogen oxides (NOx), carbon monoxide (CO), and/or particulate matter (PM-10); e.g., soot, aluminum oxide, magnesium oxide, or magnesium chloride. Where such testing is conducted at a new facility or a "modification" of an existing facility, new source performance standards will apply to emissions of NOx, CO, or PM-10 equal to or greater than 100 tons/year.

About 100 areas in the U.S. are currently classed as

"nonattainment" for ozone, about 40 for CO, and 50 for PM-10. For these nonattainment areas, the scope of regulated facilities and the nature of required controls may be dramatically expanded. Covered "major" sources must institute BACT (best available control technology) for new facilities and RACT (reasonably available control technology) for existing sources. For ozone nonattainment areas, the threshold for NOx emission control varies from 100 tons/year for "moderate" or "marginal" areas to 10 tons/year for an "extreme" area. In the case of CO, the lower limit is 100 tons/year, except in "serious" nonattainment areas where the threshold may be 50 tons/year. The PM-10 limit when considered a "major" source in a nonattainment area is 100 tons/year, unless the area is classified as "serious," in which case the threshold is 70 tons/year.

The provisions which significantly expand the list of specific pollutants covered are contained in Title III of the 1990 CAAA. Among the 189 hazardous air pollutants listed are chlorine (Cl_2) and hydrogen chloride (HCl). Facilities which emit more than 10 tons/year of any single one of the 189 pollutants or more than 25 tons/year of any combination of these substances are considered "major" sources and require permits. Moreover, Environmental Protection Agency (EPA)-designated categories of such major sources will be required to implement MACT. It should be recognized that the abovementioned 10 and 25-ton thresholds for hazardous air pollutants are eliminated under the "area source" provisions of the Clean Air Act covering hazardous air pollutants in urban areas. The 1990 Amendments

also provide that EPA shall conduct a residual risk assessment on the 189 listed pollutants and report to Congress. This may result in even more stringent health-based standards being imposed on any of these substances.

Title I of the CAAA requires that each state develop a revised State Implementation Plan (SIP) that meets with EPA approval. The SIP reflects the state's approach to implementing the CAAA and, at a minimum, must reflect all of the requirements of the CAAA. It is likely that in many states the SIP will be more stringent than the minimum federal CAAA control provisions, especially in areas presently experiencing non-attainment conditions in air quality. Tighter restrictions may be imposed on the rate of rocket launches and test firings as well as the conditions under which they can occur, due to the NOx, CO, and PM-10 emissions from the rockets.

Furthermore, each state is permitted to impose more stringent air quality standards than imposed by the CAAA. These standards may further restrict the air quality concentrations, the amount of pollutants allowed, and add to the list of air pollutants controlled.

(2) Future Regulatory Actions

As global awareness of environmental issues, buttressed by better scientific data, continues to evolve and focus on specific concerns, the space launch industry could face an increasing array of restrictions designed to mitigate or minimize its environmental impacts. Known issues such as ozone depletion and global warming will be better understood in the 1990s, and

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other environmental concerns, unknown today, may be the headline grabbers of the future.

The Montreal Protocol, for example,designed to control and eventually eliminate the use and manufacture of stratospheric ozone-depleting chlorofluorocarbons and other halogenated solvents through international agreement, could be extended to cover additional sources of these harmful chemicals. Title VI of the 1990 CAAA could be extended to do the same. The control of "greenhouse" gases such as carbon dioxide could become the subject of similar international agreements or federal legislation.

These issues require that aerospace industry officials pay close attention to growing environmental concerns and begin to integrate environmental themes not only into the early design stages of new system developments, but into their mission goals as well.

C. The Atmospheric Boundary Layer (Lower Troposphere)

   (1) Description

      The atmospheric boundary layer is the lowest portion of the atmosphere; that is, the portion in contact with the ground. It is typically one to two km in thickness, with wind and temperature structure determined by (1) the Earth's surface, through roughness and solar heating, and (2) the large-scale structure of the troposphere; e.g., inversions. Typically the boundary layer is hydrostatically stable at night and unstable during daylight hours. At sufficiently high wind speeds the boundary layer is hydrostatically neutral because it is well

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mixed.

In a hydrostatically unstable boundary layer a parcel of air at a given level will continue to move away from that level upon being vertically displaced (i.e., positive buoyancy). Unstable boundary layers typically occur on hot days and are characterized by convective mixing. In a hydrostatically stable layer a parcel of air at a given level will return to the given level after being vertically displaced (negative buoyancy). Stable boundary layers typically occur at night and during the early morning hours when there is little or no vertical mixing. Neutral boundary layers are neutrally buoyant, and result from mechanical mixing of the boundary because of mean flow wind shear. Neutral boundary layers occur on days when wind speed is relatively high; e.g., greater than 10 m/s. The mean flow and associated turbulence in the atmospheric boundary layer transport and disperse rocket plume effluents and hence determine the concentration of effluents downstream of the launch or test site.

(2) Halogens

The halogen of concern at present is chlorine, particularly hydrogen chloride gas and its liquid form, hydrochloric acid. These chemical species have the greatest potential impact on the near-field and adjacent-surface environments. The issues of acid deposition and environmental impacts have been studied extensively for the past decade.

Sufficient technical data are available for implementing operational models, with the possible exception of refinements in complex terrain-flow patterns for the various test and launch

facilities.

High-priority issues are (1) the modeling of cloud-rise vs. inversion-layer dynamics and impacts, and (2) certifying and/or verifying the validity of operations models via real-time field studies.

Other operational model issues that need to be addressed include (3) development of a model for residual hydrogen chloride (HCl) "revolatilization,;" i.e., the evolution of HCl from surfaces near the launch/test site, (4) refinement of diffusion coefficients and other model parameters based on field studies and detailed model analyses, so that the operational models are tailored to the local application (such adjustments are essential to account for complex terrain and sea-breeze effects, etc.), and (5) training and certifying personnel to run and apply the operational models.

Scientifically, the physics and chemistry of halogen reactions are generally well known, as are the basic mechanics of the dispersal process. However, additional information and data are still needed (6) to apply detailed scientific models (a) to worst-case scenarios for catastrophic events at test and launch facilities and (b) to normal test sequences, to verify that the expected cloud rise and transport will occur as expected under worst-case meteorological conditions, and (7) to model potential mitigating measures to determine their applicability.

(a) Measurements and Monitoring

Experience has shown that point-location type measurement systems are difficult and labor-intensive for the study and monitoring of gases released from a rocket launch or test. Winds

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carry the plume to locations other than that of fixed monitoring instruments, thus requiring multiple mobile monitoring stations. The application of remote sensing, either line-of-sight (lidar) or area imagery, would improve the acquisition of useful data. The application of these technologies should be investigated for routine support of operations and complement existing regulatory-mandated technologies .

(b) Acute Toxicology

Hydrogen chloride, chlorine, and the other halogen acids which are or may eventually be associated with primary rocket propulsion are common substances with well-defined toxicological properties. There exists a substantial experience base on their effects, and history has shown that the issues are manageable. Meteorological scenarios have been identified which can lead to violation of air quality standards, and operational controls have been imposed to prevent releases during these conditions.

(c) Wet Acid Deposition

Wet acid deposition (currently HCl) results mainly from the use of halogens in launch-vehicle propellants, although there is also some deposition of nitric acid (HNO_3) from NOx. Current knowledge of wet deposition due to the water deluge system at the launch pad at Kennedy Space Center is extensive, but little is known about other test facilities or other launch sites. Existing computer modeling technologies are available to develop and improve operational models designed to protect and minimize operational impacts to facilities (electronics and computers) and to identify potential threats to public property.

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(d) Effects on the Biosphere

Data on the ecological effects of HCl and other acids has been acquired and published as a result of concerns over acid rain and through monitoring activities at Kennedy Space Center. Near-field observed and potential problems include acute damage to vegetation and changes in soil structure and chemistry, alterations of soil cation exchange capacity, increased mobility of metals including aluminum, alteration of soil microbiological communities, and changes in aquatic chemistry.

Impacts are highly dependent on site-specific characteristics. Development of new facilities or propellants should be accompanied by early, site-specific assessments of potential environmental effects. Long-term, follow-up monitoring programs should be developed for each test and launch site to validate the assessments and verify predictions. Results of monitoring programs should be utilized to develop or improve mitigation strategies where appropriate.

(3) Particulates

(a) Operational Models

Particulates are transported and dispersed by atmospheric boundary-layer wind and turbulence. Current operational models for homogeneous terrain are adequate for calculation of concentration levels. Improvements for complex terrain and better diffusion coefficients need to be incorporated into operational models. The initial condition for the operational models is the exhaust plume. The subsequent behavior of the plume; i.e., vertical rise, is critical to the dispersion

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calculations and prediction of air concentrations. To assure valid application and operational decisions with sufficiently low risk, plume rise and dispersion as a function of meteorological conditions should continue to be investigated through field studies. Technically-supported modifications to the models should be made necessary, and predictive results should be certified by trained personnel.

(b) Field Measurements and Monitoring

Knowledge of the physical and chemical properties, e.g., size distribution and solubilities, is critical to the scientific and operational assessment of particulates. For example, the size distribution of Al_2O_3 and its thermodynamic phases (alpha and gamma), along with its chlorine chemistry, are critical to understanding the path of aluminum into the environment. The gamma phase is metastable, and at both low and high pH conditions may become soluble and mobile, providing a pathway into the environment. To further understand this path and define the extent and mechanisms of Al_2O_3 "chloriding," analyses of field samples from dry static firings should be made.

(c) Laboratory Measurements

To support field measurements, laboratory studies under controlled environments would provide additional data on the chemistry of Al_2O_3 "chloriding" and the associated atmospheric and terrestrial potential impacts.

(d) Toxicology (Acute)

Our current understanding of the toxicology of particulates is controversial. The knowledge base continues to be expanded through current medical research. The evolution of this field of

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medical research should be closely followed for its implications to launch-vehicle operational procedures. Issues associated with worker and public exposure and the disposition and effects of rocket-generated particulates in the environment should be closely monitored.

(e) Cumulative Effects

The cumulative effects on ecosystem impact and human health of particulates, especially Al_2O_3, along with synergistic effects, need to be further studied on existing test and launch sites.

(4) Carbon Monoxide and Dioxide

In the context of the tropospheric boundary layer, carbon monoxide and dioxide are of potential concern for local-area, short-time-scale effects. These gases from test or launch activities are not an environmental issue.

(5) Nitrogen Oxides

NOx is always present downstream of the exit plane of the exhaust nozzle because atmospheric nitrogen is entrained into the rocket plume and afterburned. Nitrogen is also present as a propellant constituent in some systems. The resulting NOx eventually will interact with the environment through a series of chemical reactions which lead to the formation of nitric acid and ozone. To understand this impact, the NOx output from the rocket plume must be quantified and the impact on the environment assessed through the application of scientific models of the atmosphere. Monitoring of relevant nitrogen chemistry products

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should be performed to verify scientific model analysis and identify the need for mitigation.

In terms of needed future effort, the measurement technology for these and other gaseous species should include investigating the use of remote-sensing systems which could potentially provide wide-area information.

(6) Trace Metals and Organics

At each test and launch facility the potential exists for the disposal and/or deposition of trace metals and organics in the boundary layer, depending on propellant and facility characteristics. The focus is on heavy metals and toxic organics which may be produced or dispersed by the launch or test process. They may derive from minor constituents in the propellants or rocket components eroded in the firing process, or from paints and construction materials eroded and dispersed from the facility. Analyses of soil samples from the launch complex areas at Kennedy Space Center indicate trace heavy-metal deposition.

Routine environmental monitoring should be conducted to identify the presence, distribution, and concentration of trace constituents. Results of these monitoring and assessment activities should be utilized to develop impact minimization and mitigation procedures where appropriate to meet regulatory requirements and prevent environmental degradation.[18]

C. Free Troposphere Impact

(1) Background

The free troposphere is the section of the atmosphere between the atmospheric boundary layer, which typically ends one

to two km above the surface, and the bottom of the stratosphere (the tropopause), which is typically ten to twelve km in altitude at mid-latitudes. This portion of the atmosphere regularly receives polluted air from the boundary layer and, less frequently, ozone-rich air from the stratosphere. Surface emissions must pass through the free troposphere on their way to the stratosphere. Photochemical oxidation, primarily by hydroxyl radicals, is an important chemical sink for many trace species in this region. In addition, significant chemical processing may occur by heterogeneous and liquid-phase reactions in cloud droplets. Most trace species processed by photochemical and/or cloud chemistry are redeposited within the boundary layer or, by precipitation, directly to the surface.

The free troposphere is the key portion of the atmosphere in regulating the radiative transport of both incoming sunshine and outgoing thermal (infrared) radiation from the Earth's surface. Both clouds and infrared-active trace gases, such as water vapor, carbon dioxide, methane, nitrous oxide, chlorofluorocarbons, and ozone, have their major effect in the free troposphere. This portion of the atmosphere is thus the critical player in the atmospheric greenhouse effect.

    (2) Status of Analytic and Predictive Models for the Free
        Troposphere

        Global two- and three-dimensional models of the free troposphere are currently under active development to assess current environmental issues such as the "greenhouse" effect and atmospheric lifetime issues, tropospheric ozone formation and destruction, and alternate chlorofluorocarbon atmospheric

lifetimes. The gas-phase photochemistry submodels are well developed and capable of handling the atmospheric chemistry of major gaseous rocket exhaust species.

Two major features of free tropospheric models require ongoing work. The first is the problem of dealing with spatially discrete trace gas inputs, rather than broad-scale boundary-layer emissions. A rocket plume is, of course, a uniquely discrete trace gas source. Large-scale free tropospheric models are being modified to include discrete emission sources by either embedded plume or subscale grid models. Such techniques should allow assessment of the impact of exhaust plumes from individual launch trajectories.

A second feature of current free tropospheric models requiring upgrade is the chemical processing due to clouds. This is an active area of research, since recent models indicate that cloud chemistry may have a major impact on free tropospheric NOx levels, ozone production, and trace organic chemical processing. Clouds, of course, are transient phenomena and, in addition to processing exhaust-plume trace species, it is possible that the excess water vapor and particulates found in exhaust trails may trigger cloud formation, just as high-altitude aircraft sometimes form persistent contrails.

(3) Photochemical Oxidation

Rocket exhaust species deposited in the free troposphere will be subject to photochemical oxidation. Oxidizable species, most specifically CO and trace hydrocarbons, will react with photochemically produced OH leading to production

of CO_2 and oxygenated organics. NOx produced by both internal combustion and afterburning will tend to form nitric acid, but will also participate in tropospheric ozone formation. Soot is also subject to oxidation reactions with OH, ozone, and NOx. Gaseous halogens not in the acid form will be photochemically cycled toward those species.

(4) Cloud Chemical Processing

Cloud droplets and atmospheric aerosols will efficiently absorb water-soluble species, including acid vapors such as HCl and HNO_3, oxygenated organics (aldehydes, ketones, alcohols, organic acids, etc.), and oxidants, including OH, HO_2, O_3, and N_2O_5. Many of these species have an active heterogenous surface and/or liquid phase chemistry. N_2O_5, formed from NOx in the free troposphere at night, forms HNO_3 on contact with aqueous aerosols and cloud droplets.

Hydroxyl and hydroperoxyl radicals and ozone can participate in the liquid-phase oxidation of SO_2 and oxygenated organics. Modeling these cloud conversion processes is important if the ultimate chemical fate of rocket exhaust species is to be assessed.

(5) Cloud Nucleation

Many portions of the upper free troposphere have low levels of cloud condensation nuclei (CCN). Aircraft exhaust trails often nucleate permanent contrails which can contain far more condensed water than the aircraft emitted. The cloud cover created by this process in heavily traveled air corridors is suspected of local weather modification.

Turco and co-workers[19] have speculated that alumina

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particles from a highly ambitious space shuttle launch program (52 launches per year, vs the currently projected 8 per year) would double the CCN content of the northern hemisphere's upper troposphere, leading to more frequent formation of high-altitude clouds with a potential impact on solar radiant scattering leading to a climatic effect. If that speculation were to be borne out, this proposed cloud nucleation phenomenon could turn out to be a significant potential environmental impact of rocket exhausts in the free troposphere for long-term future launch levels. However, detailed measurements of ice nucleus counts taken in the exhaust cloud generated by the third Space Shuttle launch from four minutes to four hours after launch showed no statistically significant difference from out-of-cloud measurements during the same period.[20,21]

(6) Required Research on Free Troposphere Issues

Based on current knowledge the major impacts of rocket exhaust on the free troposphere which need a more thorough assessment are:

(a) Cloud nucleation properties of rocket exhaust particulates, including aluminum oxide and soot produced by current solid and liquid systems. This process is presumably influenced by particle size distributions, which affect both nucleation efficiency and atmospheric residence times, as well as surface chemical properties and surface reactions leading to increased hydrophilicity. Particulates produced by advanced propellants, currently under development (e.g., magnesium chloride, sodium chloride, magnesium oxide, etc.) should also be

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assessed for cloud nucleation potential.

(b) As tropospheric ozone's greenhouse potential becomes better known, sources of mid-tropospheric NOx may come under intense investigation (particularly for liquid N_2O_4/hydrazine systems) and afterburning (all systems). In order to assess the impact of rocket-exhausted NOx a full afterburning plume calculation must be performed. This is an issue for NOx deposition in the boundary layer and lower stratosphere, as well as for the free troposphere. Model assessment of the NOx input from afterburning plume exhausts will require (i) an accurate nozzle flow and afterburning prediction of NOx production (it is kinetically controlled in both the nozzle and plume); (ii) the ability of free tropospheric models to accept a discrete line input source; and (iii) the capability for doing cloud NOx processing, as appropriate.

(7) Impact on Propulsion System Development

The developers of new and/or refined rocket propulsion systems should be aware that the particulate output, depending on its size distribution and water solubility, may have a significant impact. Assessment and, where practical, control of particulate properties should receive consideration.

Larger particles (greater than 3 microns) will in general have a smaller atmospheric impact, due to their smaller number per unit mass of exhaust and shorter atmospheric residence times. Particles with hydrophobic surfaces that remain resistant to oxidation will tend to be poor cloud condensation nuclei.

(8) Allied Research Activities

NASA is currently pursuing an intensive research program aimed at evaluating the impact of high-altitude aircraft on the lower stratosphere, and, concomitantly, the upper troposphere. This program, on the Atmospheric Effects of Stratospheric Aircraft (AESA) of the High Speed Research Program (HSRP), will gather significant data on the physics and chemistry of exhaust soot and NO_x and their impact on the upper atmosphere. Much of this work will benefit assessments of rocket exhaust plume products on both the free troposphere and the stratosphere.[22-30]

D. Stratosphere and Above

(1) Stratospheric Ozone

(a) Background

The stratosphere is the main region of ozone production in the Earth's atmosphere. It is located from about 10 to 50 km, and is marked by a temperature minimum at its bottom and a temperature maximum at its top. The partial pressure of the ozone contained in the stratosphere amounts to only about 3 mm at standard temperature and pressure, although substantial variations in the total ozone column occur with latitude (e.g., in early spring variations of over 50% are observed from equator to pole).

Stratospheric ozone absorbs ultraviolet radiation so effectively that very little radiation with wavelengths shorter than 300 nm reaches the Earth's surface. Increased ultraviolet radiation is known to increase rates of skin cancer in humans[31]

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and may produce other deleterious effects on plant and animal life. Although the effect of increased ultraviolet radiation on aquatic ecosystems is not well known, it is of particular concern in the vicinity of Antarctica, where ozone reductions have been particularly large.

At any particular location the concentration of ozone results from a dynamic balance between the ozone transported by stratospheric circulations and ozone destruction and production by chemical means. This balance is nonlinear, as there is a subtle interplay between ozone chemistry and the mean circulation, each affecting the other. The exact nature of the ozone budget depends on the particular atmospheric location: the stratospheric circulation transports ozone from where it is produced, primarily in the equatorial regions in the middle and upper stratosphere (where the ozone balance is primarily of a chemical nature) to all other regions of the stratosphere (where the atmospheric circulation plays an important role in the ozone budget).

The dynamic nature of this balance implies that ozone can vary on many timescales. Variations on timescales of up to 11 years are observed, correlated with the solar cycle. Annual variations in the total global ozone column can be up to 1%, while day-to-day changes in the total column ozone can be greater than 10%. Causes of temporal ozone variations include changes in ozone transport, changes in ozone chemistry, or a coupling between these processes. Variations in ozone chemistry may be solar-related or caused by other natural or anthropogenic variations in the chemistry of the stratosphere.

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Ozone (O_3) is continually being produced and destroyed. Production of ozone is controlled by photodissociation of molecular oxygen (O_2). Ozone destruction is controlled by various photochemical cycles, most involving a catalytic process. For example, a chlorine atom can be responsible for the destruction of several hundred molecules of ozone through the process:

$$Cl + O_3 \longrightarrow ClO + O_2$$

followed by

$$ClO + O \longrightarrow Cl + O_2$$
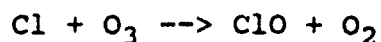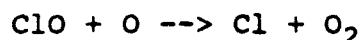
Note that Cl is not destroyed in these two reactions, and the cycle continues until Cl reacts with another atmospheric constituent. As an example of the latter process, Cl may react with methane (CH_4) and be converted to the reservoir species HCl. Reservoir species are not involved in the catalytic loss of ozone. However, the chlorine contained in these species may be converted back to an active radical form which is again capable of destroying ozone. Reservoir species may also be transported to the troposphere where they can be lost in rainout processes. Typical residence times for Cly (Cl, ClO, HCl, HOCl, and $ClONO_2$) can be estimated at two to three years.[32]

The most important families involved in ozone loss include Ox (O_3 and O), HOx (H, OH, and HO_2), NOx (NO and NO_2), Clx (Cl and ClO), and Brx (Br and BrO).[33-35] These families do not react independently; constituents of one family react with constituents with other families (e.g., NO_2 can react with ClO to form the reservoir species $ClONO_2$). Both natural and anthropogenic

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processes produce long-lived source gases which are transported to the stratosphere where they form the various family constituents involved in the ozone budget.[33] The stratospheric circulation plays an important role in determining the distribution of these constituent families.

In addition to the homogeneous chemistry described above (gas-phase chemistry only), recent work has indicated the importance of heterogeneous chemistry on the ozone budget (gas-phase reactions with liquid or solid particulates). In particular, the formation of the Antarctic ozone hole can only be explained if heterogeneous processes are considered.[34] The formation of ʻolar stratospheric clouds at the extremely low temperatures of the Antarctic winter is thought to be crucial to the heterogeneous processes,[34] acting to denitʻify the Antarctic polar vortex while converting chlorine compounds into an active form.

It is believed that increases in chlorine levels caused by anthropogenic activities are directly responsible for the ozone hole. Laboratory measurements indicate that some of the same heterogeneous reactions which occur over Antarctica can also occur on sulfuric-acid particles.[36-38] A modeling study[39] shows that the combination of the enhanced stratospheric chlorine levels due to anthropogenic activities and background levels of stratospheric sulfuric acid aerosols substantially reduces the level of stratospheric ozone. Enhanced aerosol levels due to large volcanic eruptions may magnify the ozone reduction. It has been suggested[40] that large ozone reductions may occur after volcanic eruptions.

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Recent observations and analysis have indicated a substantial reduction (2-3%) in global total ozone over the past 11 years[41]. This trend is particularly large near the Antarctic continent (associated with the ozone hole), -3.0% per year. However, significant ozone losses have also occurred between 40 and 50°N, with trends of -0.2% per year in summer and -0.8% per year in winter. Particularly alarming is that the rate of ozone decrease appears to be accelerating in recent years. Calculations including heterogeneous chlorine chemistry on sulfuric acid aerosols give results which may explain the observed ozone trends in the Northern Hemisphere middle latitudes[42]. Concerns about the ozone layer and in particular the effects of anthropogenic chlorine on the ozone layer have led to the Montreal Protocol calling for a gradual phasing out of many chlorinated species.

Due to the complicated coupling between chemistry and atmospheric transport, the effect of anthropogenically induced changes in stratospheric ozone is usually studied with complex numerical models. These models range from box photochemical models to three-dimensional (3D) general circulation models. The lower-dimensional models usually describe the chemistry more completely, but have simplified transport processes. Transport processes are best represented in 3D models, but the chemistry is highly simplified. Thus, all models treat the atmosphere in a highly simplified form and their results should be taken with some caution.

Most assessments of the influence of anthropogenic changes

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on the stratosphere chemistry are carried out with 2D models, whose dimensions are latitude and altitude. These models contain approximately full homogeneous chemistry, but heterogeneous chemistry is generally not included and the transport processes are highly simplified. To understand the effect of chemical exhaust on stratospheric ozone it is necessary to use models which take into account the chemical make-up and radiative effects of rocket exhaust, as well as stratospheric chemical reaction rates and transport processes.

(b) Effect of Chemical Rockets on Stratospheric Ozone

(i) Introduction

The major chemical effluents of rocket exhaust that can potentially perturb stratospheric ozone include chlorine compounds (HCl and Cl_2), nitrogen compounds (NO), and hydrogen compounds (H_2 and H_2O). Each of the radicals (Cl, H, OH, HO_2 and NO) formed directly or indirectly from rocket exhaust can cause the catalytic destruction of ozone. In particular, assuming nine Shuttle launches and six Titan rockets per year, 0.79 ktons of chlorine are released into the stratosphere every year by rockets (compared with 300 ktons released by all industrial sources). The introduction of chlorine into the stratosphere by rockets is larger if we include the European Ariane.

Other exhaust compounds which could presumably lead to ozone destruction either by direct reaction with ozone or by providing a surface for heterogeneous processes include the particulates Al_2O_3, ice, and soot. Several studies have been completed on the influence of rockets on stratospheric ozone.[4,5,7-10,43-46] None

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of the studies include the full complement of chemical species emitted by chemical rockets (HOx, Clx, and NOx). In addition, and very importantly, none of these studies include heterogeneous processes.

(ii) Local and Regional Effects

It has been suggested that substantial local reductions in ozone are possible.[47] Measurements of ozone loss in the exhaust trail of a Titan III solid rocket at an altitude of 18 kilometers only 13 minutes after launch indicate that ozone was reduced by more than 40% below background.[43]

Detailed model computations of the local impact of a single launch of both the Space Shuttle (solid and liquid propellants) and the Soviet Energiya (liquid propellants) have corroborated these measurements of ozone loss from rocket launches.[9] The modeling study included the effects of chlorine species (from the Shuttle) and nitrogen species (from the Shuttle and Energiya). Local (within 1 km of the exhaust plume) ozone decreases are found to be very large (>80%) due to the modeled chemistry (Clx and NOx chemistry) between one and three hours after launch, and are approximately the same for both launch systems. As the launch trajectories are not vertical, the total column ozone decrease at any location is computed to be less than 10%. Recovery to near background levels of ozone occurs in three hours at all levels in the stratosphere. However, the exact recovery time is very dependent on the parametrized transport processes in this model.

These calculations are supported by the Nimbus 7 satellite

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Total Ozone Mapping Spectrometer (TOMS) instrument measurements which show no detectable total column ozone reduction over the area around the Kennedy Space Center several hours to one day after a Space Shuttle launch.[48] These measurements are calibrated to detect about a 3-4% ozone decrease in an area 40x40 km.

Regional effects (1000x1000 km) due to rocket effluents have been computed, for Clx homogeneous chemistry only, from a single Space Shuttle launch using a 3D model.[4,5] The Clx concentration at 40 km, 30^ON, 70^OW can increase by a few percent two days after the launch and the corresponding ozone decrease is expected to be less than 1%. The Clx emitted by the Shuttle becomes spread over all longitudes in about 30 days.

(iii) Global Effects

Global effects on Clx and ozone due to rockets, as affected by Clx homogeneous chemistry, have been computed using 2D models. The steady-state impact of nine Space Shuttles and six Titan IV launches per year were assessed by 2D models.[4,5] Clx increases were computed to be at a maximum of 0.5% in the stratosphere between 30 and 60^ON. Corresponding maximum ozone depletion was calculated at less than 0.2% at 40 km in the winter hemisphere. Maximum total column ozone depletion is less than 0.1%.

Using the same launch scenario, a computation of the total global stratospheric ozone depletion is found to be about 0.0065%.[49] The global effects of Space Shuttle launches have also been computed by another atmospheric modeling group.[9] Scaling their calculations to an equivalent nine Shuttle and six

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Titan launches per year gives a total global ozone depletion of 0.0072 - 0.024%.

Another steady-state model computation which assessed the impact of the chlorine released during ten Ariane-V launches per year over 20 years has also been undertaken.[10] Preliminary computations indicate an effect similar to that computed above for Shuttle and Titan launches (e.g., maximum local ozone depletion is around 0.1% near 40 km).

With one exception,[9] all modeling studies discussed above consider only the effect of the chlorine emitted from the rocket exhaust. None of the studies considers HOx, NOx, and Clx in conjunction. A calculation of the relative contributions of nine Space Shuttle and six Titan IV launches to the stratospheric burdens of the other potential ozone-destroyers HOx (from emitted H_2 and H_2O) and NOx (from emitted NO), as well as Clx, has been completed.[46,50] In this computation, NOx was increased by 0.0014% (though no NOx production from afterburning was considered), HOx was increased by 0.0048%, and Clx was increased by 0.16%, all above the global background. If the NOx production from afterburning as estimated by Karol et al.[9] is correct, the perturbation to stratospheric NOx would be about 0.02 - 0.09%. These calculations indicate that the rocket induced Clx changes should be the most significant when considering stratospheric ozone.

A computation has recently been completed on the effects of HOx from a hypothetical National Aerospace Plane (NASP) on stratospheric ozone.[51] A rate of forty launches/year results in

H_2 and H_2O increases of 0.34% and 0.16%, respectively, at 35 km altitude and 35^ON latitude. This results in an OH increase of 0.1% and a corresponding ozone decrease of 0.006% at this location. Total global column ozone impact is calculated to be a decrease of less than 0.0002%.

(iv) Summary

Rocket launches can have a significant local effect on the stratosphere by reducing ozone substantially (perhaps >80%) within a kilometer of the exhaust plume up to three hours after launch. However, none of the atmospheric modeling studies which assume the present rate of rocket launches (of one country only) show a significant global impact of rockets on the ozone layer (the calculated impact is much smaller than the effect of the solar cycle on ozone, for instance). These modeling studies are incomplete and may underestimate the ozone depletion expected by rockets. For instance, none of the above studies consider the potential impact of heterogeneous chemistry.

The inclusion of heterogeneous chemistry can affect the results discussed above in several ways. First, it has been predicted[39] that heterogeneous chemistry can enhance the ozone decrease by chlorine species even in the absence of polar stratospheric clouds. Secondly, the particulates emitted by rockets can provide additional surfaces on which heterogeneous chemistry may occur. Rough estimates suggest that rockets increase the aerosol surface of the unperturbed stratosphere by about 0.1%.[5,46] However, at present not much is know about the possible effects of these particular exhaust particulates on heterogeneous ozone chemistry. Finally, the particulates

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released by the rockets themselves may chemically react with ozone. Again, these reactions are not known.

(2) Other Effects: Radiative; Region above the Stratosphere

Rockets also have an impact on the Earth's radiation budget, both by changing the chemical composition of the stratosphere and by releasing aerosols. Rockets emit greenhouse gases into the stratosphere as well as water vapor. The net climatic impact of these effluents is unknown, but is expected to be small.

The Space Shuttle's solid rockets deposit their effluents primarily in the troposphere and stratosphere, but the Shuttle's main engines (liquid-propellant) deposit their effluents (primarily H_2 and H_2O) above 50 km in the mesosphere and ionosphere. Detailed model simulations of these effects have not been completed. It is expected that local and regional effects could be significant in the mesosphere and ionosphere since the atmosphere is quite tenuous and the depositions of H_2 and H_2O are substantial (see Table 4 in Section III). Large effects in the ionosphere from the launch of a chemical rocket have even been observed.[52] These effects should be characterized in future studies.

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APPENDIX

1. Steering Committee Members

Mr. W. Geary Andrews
Aerojet Propulsion Division

Dr. Frank G. Collins   Alternate: Dr. George Garrison
University of Tennessee   University of Tennessee
  Space Institute   Space Institute

Dr. John Daily
University of Colorado at Boulder

Mr. Thomas L. DuBell
Pratt & Whitney

Dr. George Fichtl
NASA Marshall Space Flight Center

Dr. Joseph Flannagan   Alternate: Charles K. Kraus
Rocketdyne Division   Rocketdyne Division
Rockwell International   Rockwell International

Dr. Jerry Grey
AIAA

Dr. Clark Hawk (Chairperson)
University of Alabama at Huntsville

Dr. Rebecca C. McCaleb
NASA Marshall Space Flight Center

Mr. John P. McCarty
NASA Marshall Space Flight Center

Mr. Allan J. McDonald
Thiokol Corporation

Dr. J. Michael Murphy
Martin Marietta Corporation

Mr. Richard Niedzwicki
NASA Lewis Research Center

Mr. Wayne Pritz
Phillips Laboratory, AFSC

Mr. W. Buzz Wells
Phillips Laboratory, AFSC

2. Workshop Participants

I). <u>Criteria</u> <u>for</u> <u>Minimum</u> <u>Environmental</u> <u>Impact</u>

Dr. Rebecca C. McCaleb (Chairman)
NASA Marshall Space Flight Center

Mr. Steven Aftergood
Federation of American Scientist

Dr. Robert R. Bennett
Thiokol Corporation

Dr. Ed Cake
Gulf Coast Group of Sierra Club

Mr. Stephen Cavanaugh
NASA Headquarters

Ms. Ellen Eagan
Sverdrup Corp.

Dr. Donald Ermak
Lawrence Livermore National Lab.

Dr. George Fichtl
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Dr. Peter Hess
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Dr. Charles Jackman
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II). <u>Liquid</u> <u>Propellant</u> <u>Rockets</u>

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Mr. Stephen R. Cavanaugh (Chairman)
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Mr. Robert L. Taylor
Aerojet Propulsion Division

Mr. J. David Weiland
Martin Marietta Astronautics Gp.

Mr. W. Buzz Wells
Phillips Laboratory, AFSC

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3. Workshop Agenda

FIRST DAY - FRIDAY, June 28, 1991

0800: Registration

0830: **Plenary Session.** Welcome: Clark Hawk, Chairman

0835: Workshop Goal and Background: Clark Hawk

0845: Summary of Rocket Propulsion

      (1) Summary of Solid Rocket Propulsion, by
          W. Buzz Wells, Phillips Laboratory

      (2) Summary of Liquid Rocket Propulsion, by
          Henry Wieseneck, Rockwell International

0915: Current Status of Pertinent Regulations

      (1) International: The Montreal Protocol, by
          Dr. Rebecca McCaleb, NASA MSFC

      (2) Federal/State/Local: The Clean Air Act/Amendments
          by Ken Kumor, NASA

1015: Break

1030: Review of Atmospheric Processes

      (1) Stratospheric Effects of Chemical Rocket Propulsion,
          by Dr. Charles Jackman, NASA GSFC

      (2) Troposphere Modeling, by Dr. Jeffrey Anderson,
          NASA MSFC

      (3) Particulates, by Dr. George Fichtl, NASA MSFC

1200: Current Research and Strategies, by Allan McDonald, Thiokol

      (1) Present status of understanding
      (2) Propellants and materials
      (3) Mathematical models
      (4) Magnitude estimates

1245: Luncheon Speaker: "Public Concerns and Issues", by
      Steven Aftergood, Federation of American Scientists

1330: Workshop Procedures: Jerry Grey

1400: **Working Group Meetings** (Concurrent):

        (1) Criteria for Minimum Environmental Impact
            Chairperson: Rebecca McCaleb, NASA JSSC
        (2) Liquid-Propellant Rockets
            Chairperson: John McCarty, NASA MSFC
        (3) Solid-Propellant Rockets
            Chairperson: Allan McDonald, Thiokol

1730: **Plenary Session**: Working-Group Reports

1830: Break

1930: **Working Group Meetings** (Optional)

SECOND DAY - SATURDAY, June 29, 1991

0800: **Working-Group Meetings** (All day): Draft report. Each
      working-group report will address the following in its
      subject area:

        (1) What we know
        (2) What we <u>need</u> to know
        (3) What research must be performed or information
           developed to find out what we need to know
        (4) What action is required, and who (or which
           agency) should take that action

1200: **Plenary Session**: Working-Group Reports

1300: Adjournment

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JOANNE: Here's the new setup on the tables and figures:

Section II:
     Table 1. I have revised Table 1 (see text).
     Figure 1. Eliminate (I've included it in Table 1)

Section III.
     Figure 1 is new. It can be copied directly from the new AIAA
book, "International Reference Guid to Space Launch Systems, by
Steve Isakowitz. Just copy the two pages marked "Launch Vehicles
Overview," pp. 2 and 3 of Isakowitz, and mark on them, "Figure 1"
and "Figure 1 (Continued)"

     Table 2: Murphy's Table I (Now on two half pages; reorganize
into 1 or 2 pages)

     Table 3: Murphy's Table II

     Table 4: Murphy's Table III (3 pages); delete "(References
1, 2, and 3)" from title, and also delete footnote on 3rd page.
I've handled the references in the text.

Section IV:
     Table 5: Murphy's "Suggested Table for Exhaust Quantities in
the Solids Section"

     Table 6: Old Table 7 (Pathways) - see McDonald's corrections
(faxed to you Monday).

     Table 7: Old Table 8 (Hybrids -- corrected in text)

Section V:
     Table 8: Old Table 10 (you corrected it in the text)

     Table 9: Old Table 11 (Percent of Effluents -- I've
corrected it in the text)

     Table 10: Murphy's "Suggested replacement for Table 12 in
the Liquids section" (2 pages)

     Table 11: Old Table 13 (emissions for 3 primary propellants)

Section VI:
     Table 12: Old Table 2 (Categories of exhaust products)

Also, I HAVE NOT deleted your printing codes from the Appendix or
from (new) Table 8. I hope that won't give you trouble. All other
print codes have been cleaned out.

Call me if you have any questions. This should go out BY EXPRESS
as soon as possible.

Anane 5 (based on 9 launches per year)	CO	1,027
	CO_2	151
	H_2	89
	H_2O	403
	N_2	373
	HCl	900
	OH	1 3
	H	1 3
	Al_2O_3	1,287
H-2 (based on 2 launches per year)	CO	107
	CO_2	16
	H_2	9
	H_2O	42
	N_2	39
	HCl	93
	OH	0 1
	H	0 1
	Al_2O_3	134
TOTALS	CO	5,531
	CO_2	811
	H_2	479
	H_2O	2,169
	N_2	2,020
	HCl	4,841
	OH	7 0
	H	7 0
	Al_2O_3	6,931

TABLE 6
SOLID PROPELLANT FORMULATION PATHWAYS TO REDUCED ENVIRONMENTAL IMPACT

PROPELLANT OPTION	ACID RAIN	OZONE DEPLETION	*EFFECTS ON* TOXICITY	PARTICULATES	IMPORTANT CONSIDERATIONS*
Current booster Propellants (Baseline)	Exhaust ~21% HCL; local acid rain	Stratosphere exhaust is ~5-3 mole % HCl, 14.3 H2O, 1.59 H2, 0.25 Cl2	HCl; CO (may be burned) Al2O3 (toxicity disputed)	Al2O3 particulates, H2O (ice)	Baseline performance
Reduced AP propellants (replace some AP with non-Cl oxidizers)	~5-10% HCl; (50-75% acid reduction)	~1-3 HCl to stratosphere, potentially lowered; higher H2O & H2	Lower HCl	Al2O3 particulates, unchanged H2O (ice)	Lowered performance, near-term availability
Existing high-energy propellants (e.g., XLDB, NEPE)	~3% HCl; (~85% acid reduction)	Much lower stratospheric chlorine injection, potentially higher H2O & H2	Lower amounts of HCl	Al2O3 unchanged, H2O (ice)	Increased hazard potential. Available now
Scavenged propellant (NaNO3, AP equimolar)	<1% HCl (~95% acid reduction)	Sodium chloride in stratosphere; effect on ozone unknown but probably slight H2O & H2	Lower toxicity	Al2O3 unchanged. Sodium chloride (effect unknown) H2O (ice)	Reduced performance; needs development
Neutralized Propellant (Magnesium replaces Aluminum)	<1% HCl, (~95% acid reduction)	MgCl2, MgO in stratosphere, effect unknown but probably small	MgCl2, MgO benign	MgCl2, MgO particulates instead of Al2O3; H2O (ice)	Reduced performance Needs development
Chlorine Free Propellants (Ammonium Nitrate oxidizer)	Zero HCl, very low or no acid rain	No chlorine; no harmful species -H2O, -H2	No significant toxic species	Al2O3 or MgO, MgCl2 H2O (ice)	Reduced performance Needs development.
Chlorine Free Propellants (Hydroxyl ammonium nitrate oxidizer)	Zero HCl, very low or no acid rain	No chlorine, -H2O, -H2	No significant toxic species	Al2O3 unchanged, H2O (ice)	Needs considerable development
Chlorine-free (oxidizers)	Zero HCl, very low or no acid rain	No chlorine, -H2O, -H2	No significant toxic species	H2O (ice), Al2O3	Needs development

MEMORANDUM FOR DTIC   21 September 2016

FROM: AFRL/RQON (STINFO)

SUBJECT: Change Distribution to Distribution Statement A for TR number ASC-TR-94-9302 (ADB191722)

Responsibility for the subject report was transitioned from legacy directorate, ASC, to new controlling DoD office AFRL/RQH. Robert A. Mercier in AFRL/RQH, working with RQ Functional Arear Records Management (FARM) personnel, coordinated and managed a Freedom of Information Act (FOIA) request for the subject report, determining that the entire report was publicly releasable.

The report has been cleared through the 88ABW Public Affairs Office (clearance number 88ABW-2016-4327, assigned on September 8, 2016).

When initially published, distribution statement C had been assigned to ASC-TR-94-9302. Now, the report should be assigned Distribution Statement A and the distribution statement should read:

DISTRIBUTION STATEMENT A: Approved for public release. Distribution is unlimited.

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ROUSH.RICHARD.V.
1262988186

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Richard V. Roush
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